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PLUTONIUM RECOVERY AT THE LOS ALAMOS SCIENTIFIC LABORATORY

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ABSTRACT

Plutonium-bearing residues created in the many research and development programs at the Los Alamos Scientific Laboratory are extremely varied in type of contaminant as well as in the nature of residue. The recovery and purification of the plutonium in these residues requires, therefore, the use of a number of processes.

Research programs have led to the adoption of procedures for all phases of plutonium recovery and purification. This report discusses some of the many procedures required to recover and purify the plutonium contained in the residues generated by the research, process development, and production activities of the Los Alamos Scientific Laboratory. The report also discusses general plant facilities, the liquid and gaseous effluents, and solid waste management practices at the New Plutonium Facility, TA-55.

Many of the processes or operations are merely steps in preparing the feed for one of the purification systems. For example, the plutonium is currently removed from noncombustibles in the pickling operation with an HNO_3 leach. The HNO_3 leach solution is the product of this operation and is sent to one of the nitrate anion-exchange systems for concentration and purification.

The experimental work which led to the selection of specific operating conditions is described in LASL reports and documents listed in the bibliography.

PLUTONIUM RECOVERY AT THE LOS ALAMOS SCIENTIFIC LABORATORY

INTRODUCTION

Plutonium residues have been processed at Los Alamos since 1943. The first large scale processing was done in facilities built on DP Mesa in 1944-45. These facilities and the early flowsheets are described in LA-3542.[18] In 1969 we decided to design and build new facilities incorporating the latest technology. We selected a site on another mesa that has now been designated as Technical Area 55 (TA-55), and the facility has been give the name of Plutonium Facility (PF). An aerial view of the completed facility is given as Figure 1.

The site consists of twenty-one acres within the boundaries of the Los Alamos Scientific Laboratory (LASL). This location was chosen because of its isolation from population centers and its proximity to existing liquid waste treatment facilities.

FACILITY CRITERIA

The facility was constructed in accordance with the criteria published in the Department of Energy document ERDAM 6301. This document has criteria for site, building, and equipment construction as well as operation. These criteria cover earthquake, tornado, wind, fire, ventilation, radiation exposure, liquid and gaseous effluents, and solid wastes.

The facility is composed of several buildings in support of the process building. The support buildings do not contain plutonium and are designed only to the Uniform Building Code for commercial buildings. The process building, designated PF-4, along with the Control Room and the emergency generator building, are the only ones designed to the special criteria that will be discussed here.

SEISMIC

The major geologic features of the Los Alamos area are the Jemez Mountains to the west, the plateau area that has been cut into flat-topped land areas called mesas, and the Rio Grande Valley to the east. The plateau area is volcanic ash from the volcanoes that formed the Jemez Mountains. There is no geologic evidence that intensive earthquakes have occurred within the recent geologic history. PF-4 was designed, based on intensive studies of the site, to withstand horizontal ground motions of 0.17 g for the Operating Base Earthquake (OBE) and 0.33 g for the Safe Shutdown Earthquake (SSE).

WIND AND TORNADO

PF-4 was designed to withstand the forces induced by the Design Basis Tornado as defined in ERDAM 6301. This includes a 200 mph (96 m/s) wind, a tornado propelled light weight, high-velocity missile for penetration, and a massive, low-velocity missile for crushing effect. A section of a wall similar to that of the PF-4 walls was tested at the Sandia Laboratory in Albuquerque, and the tests confirmed design calculations. The penetration test at Sandia was done with a board that was 2 inches by 12 inches and 12 feet long on a rocket sled. The sled reached a velocity of about 160 miles an hour, and the wall made sawdust out of the board.

FIRE

The exterior walls, roof, and floor elements of PF-4 provide at least 4-hour fire resistance. The building and all components therein were constructed with a minimum of combustible material. Inside PF-4,

work areas of less than 40,000 square feet were created by construction of 4-hour fire walls. The combustible loading in the work areas, both in and out of the gloveboxes, is kept to an absolute minimum, so much so that it was difficult to find a combustible loading on which to do the safety analysis. The buildings are equipped with sprinkler systems as added protection.

RADIATION PROTECTION

The plutonium work in PF-4 is done mainly in gloveboxes. In order to achieve the design criteria of 1 rem per year per worker, the boxes were spaced seven feet apart to minimize "cross-talk" between boxes. In addition, each process was studied to determine the type and amount of shielding necessary to hold the radiation exposure to less than 1 rem per year per worker. Therefore, all gloveboxes are of a "sandwich" construction, 3/16 inch thick stainless steel followed by 1/4 inch thick lead and 1/16 inch thick stainless steel. In certain areas, 4 inches of hydrogenous shielding was added to reduce neutron radiation exposures of the workers.

VENTILATION

The air handling in PF-4 is divided into 4 systems so that air moves from the outside to corridors, to rooms, and then to gloveboxes following the principle of air going from least contaminated area to most contaminated area.

Room air is recirculated after passing through a roughing filter and a set 2 HEPA (High Efficiency Particulate Aerosols) filter stages in series. Ten percent of the recirculated air is discharged to the atmosphere through

another 2 HEPA filters. The air concentration of plutonium at the stack is less than 0.009 percent of the MPC for the air concentration values as listed in DOEM 0524 Annex A, Table II, Column I, for soluble plutonium. The concentration at the site boundary is several orders of magnitude lower.

Process air is recirculated to gloveboxes with non-aqueous processing after being passed through 3 stages of HEPA filters. The air from gloveboxes containing aqueous processes is discharged to the atmosphere after passing through 3 stages of HEPA filters. Each of the 4 process wings has its own process air ventilation system. The air is sampled continuously and found to average less than 0.009 percent of MPC.

The other 2 air handling systems involve the air that is supplied to the plant via plant corridors and the air in the basement area surrounding the other air handling systems.

LIQUID EFFLUENTS

The TA-55 plant has 4 independent liquid discharge systems. Each of them is monitored for radioactive material content.

The sanitary wastes are collected by a network of small lines that lead to the large line that serves only this site. This line is monitored by a gamma system to detect a plutonium release of 0.1 gram.

The industrial waste line collects the waste from janitor's mop sinks, decontamination showers, circulating water overflows and drainings, and sinks in laboratories that do not handle radioactive materials. The collector lines lead to a main line that is monitored by a gamma system to detect a plutonium concentration of 0.01 mg/ℓ. The data collected during the first 2 years of operation have shown that this waste solution has an average concentration of much less than 0.001 mg/ℓ.

This solution goes to a waste treatment plant where it is treated to reduce the alpha contamination to 200 d/m/ℓ.

The other two liquid discharge streams are called process waste acid and process waste caustic. These are process solutions that are collected and sampled before discharging to the waste treatment plant via dedicated lines.

The process waste caustic solutions come from hydroxide scavenging of Pu and Am from solutions that are not compatible with the high nitric acid systems in the plant and the stainless steel equipment in the plant. The chemistry of the processes will be discussed later.

The process waste acid solutions are generated as vacuum seal water, various scrub solutions, low-acid distillate from the acid recycle evaporators, and other low Pu-acid solutions. These processes are discussed later in this report.

SOLID WASTES

Solid wastes are collected, segregated, measured for Pu content with various non-destructive assay instruments, and classified into 3 categories.

A Multi-Energy Gamma Assay System (MEGAS) has been developed at LASL to measure the plutonium content of low-density wastes. In general, these are room generated wastes. This instrument is presently being used to determine if the waste contains less than 10 nCi Pu/g. We have determined that this instrument can quantitatively measure 1 nCi Pu/g or about 0.14 mg of Pu that is 6 percent ^{240}Pu.

Thermal Neutron Coincident (TNC) counters and Segmented Gamma Assay (SGS) instruments are used for measuring the plutonium content of mate-

rials that have a high density or that have a plutonium content greater than 10 nCi/g. In general, these are wastes and residues that have been generated inside the gloveboxes.

Wastes that contain less than 10 nCi Pu/g can be packaged in cardboard boxes and sent to land-fill burial. If we could not measure the plutonium content at this level, then all solid wastes would have to be packaged for placement in 20-year retrievable storage. Packaging for placement in 20-year retrievable storage is much more stringent and costly in terms of both storage space and cost of containers. These containers usually consist of a heavy wall plastic liner inside of a 200 liter steel drum. These drums are placed in controlled areas that are prepared so that the drum can be retrieved 20 years later with the external surface still free of contamination.

Wastes with a recoverable amount of plutonium are sent to the appropriate recovery process as shown in Figure 3.

PROCESS BUILDING

The process building is called PF-4. A line drawing of this building is given as Figure 2. Each of the 4 process areas is served by an overhead conveyor that connects each glovebox line to one another and to the material management room at the end of each wing. These material management rooms are connected by a conveyor, thus making it possible to transfer items from one process area to another without doing bag-out operations, and this reduces the quantity of waste generated.

The gloveboxes and equipment are designed to provide surfaces that are accessible and easy to decontaminate. It is our design philosophy to install multiple, small process units rather than one large unit that is hard to decontaminate.

PROCESSING

The residues that contain an economically recoverable amount of plutonium are processed according to the flowsheet shown in Figure 3. The basic plan is to get the residues to a physical state that is amenable to safe, efficient acid leaching or dissolution giving a solution that contains nearly all of the radioactive material. The Pu in these solutions can then be recovered and purified by 3 methods, either alone or in combination; solvent extraction, ion exchange, and precipitation. We want to recover as much plutonium as possible with a minimum of effort while generating the least amount of residues that would have to be treated, stored, or discarded.

For example, all of our process rags are burned in an incinerator at a low temperature to produce an ash that can be dissolved in HNO_3 - CaF_2 according to the process shown in Figure 4. The resulting solution is transferred to an ion-exchange system where the plutonium is concentrated and purified using the procedure shown in Figure 5.

The effluents from the ion exchange columns are 7 M HNO_3 and contain from 1 to 10 mg Pu per liter and a large quantity of nitrate salts. In the past these solution were neutralized, mixed with cement, and the slurry placed in galvanized containers which could be placed in retrievable storage when the slurry solidified. When our new plutonium facility was under design, we decided that this process should be replaced. Therefore, we designed and installed thermo-siphon evaporators that would remove the acid, concentrate the nitrate salts, and prepare the acid distillate for re-use.

The flowsheet for this process is given in Figure 6. Evaporator number one distills about 95 percent of the anion exchange effluent. The

bottoms from evaporator number one are drained, while thermally hot, into a slab tank and allowed to cool. As the bottoms cool, nitrate salts are formed, mainly Ca, Mg, and Al, and these salts contain less than one percent of the radioactivity in the original effluent. The nitrate salts make up about half of the volume of the cooled bottoms. The other half is a clear supernatant that contains some nitrate salts and greater than 99 percent of the radioactive material. The nitrate salts that are present prevent efficient recovery of the plutonium and americium by ion exchange. We are installing solvent extraction equipment using di-Butyl-Butyl-Phosphonate in kerosene to extract the Pu and Am and leave the Fe and Pb in the raffinate. In the meantime, we are neutralizing the supernatant with NaOH until the Pu, Am, and Fe precipitate as hydroxides. After filtering, the hydroxide cake is mixed with cement and prepared for packaging and storing as retrievable waste. The hydroxide filtrate contains less than 1 mg/ℓ total alpha activity, and this solution is transferred to the waste treatment plant via the dedicated process waste caustic line.

The distillate from evaporator number one is fed to evaporator number two where water and some acid can be removed by distillation leaving the bottoms 10 $\underline{M}$ in HNO_3. The distillation is continued until a spot sample of the evaporator two distillate is found to be 4 $\underline{M}$ H^+ by titration with NaOH. Experiments have shown that when the distillate reaches 4 $\underline{M}$ in H^+, the bottoms will be $\sim$ 10 $\underline{M}$ in H^+. The 10 $\underline{M}$ HNO_3 is placed in tanks that are piped to each glovebox in the recovery facility so that the acid can be re-used. The distillate from evaporator number two has averaged 3 $\underline{M}$ H^+ and less than 0.1 mg/ℓ total alpha activity. This distillate is transferred to the waste treatment facility via the dedicated process waste acid line.

Other residues that require treatment before the plutonium can be sent to plant processes include chloride solutions and chloride melts.

The chloride solutions that are generated in various metal pickling operations or in certain analytical procedures are processed with a ferric hydroxide carrier precipitation. The flowsheet for this process is shown as Figure 7. The hydroxide cake is dissolved in HNO_3 - HF (see Figure 8) and sent to an anion exchange system for recovery of the plutonium. The chlorides are discarded in the caustic solution via the dedicated process waste caustic line.

The chloride melt from the purification of plutonium metal by electrorefining contains a recoverable amount of plutonium. This melt can be dissolved in dilute HCl or HNO_3, but the resulting solution is not compatible with stainless steel equipment, especially items such as evaporators. Therefore, such solutions should go to a hydroxide precipitation system as was previously discussed. That process will separate the plutonium and americium from the chloride, but doing it that way generates much more liquid waste than dissolving the chloride melt directly in KOH or NaOH. The halides dissolve while the plutonium and americium precipitate as the hydroxides.

Filtration then yields a small volume of caustic filtrate to be sent to final waste treatment. The hydroxide cake is dissolved in HNO_3 - HF to give a feed solution suitable for purification by ion exchange in glass and stainless steel equipment.

Another class of residue that requires special head-end treatment is the plutonium-beryllium neutron source. The sources have neutron radiation levels in the 10^6 - 10^7 n/s range. These must be processed behind special shielding until the plutonium and beryllium are separated. The

process must remove the beryllium and keep it separated from the plutonium until the beryllium can be discarded. The process developed for this purpose is shown in Figure 9.

Processes for other residues have been discussed in a document "Plutonium Processing at the Los Alamos Scientific Laboratory."[18]

SUMMARY

The Plutonium Facility, its equipment and processes, have been designed to recover as much plutonium as possible while minimizing radiation exposure to the workers.

The plant and its processes have also been designed to minimize the generation of liquid and solid wastes that require further treatment before disposal or retrievable storage. The use of conveyors to transfer material between process units and the recycle of nitric acid are major components in this program.

Further reduction in radiation exposures and amount of wastes generated are being sought in development programs.

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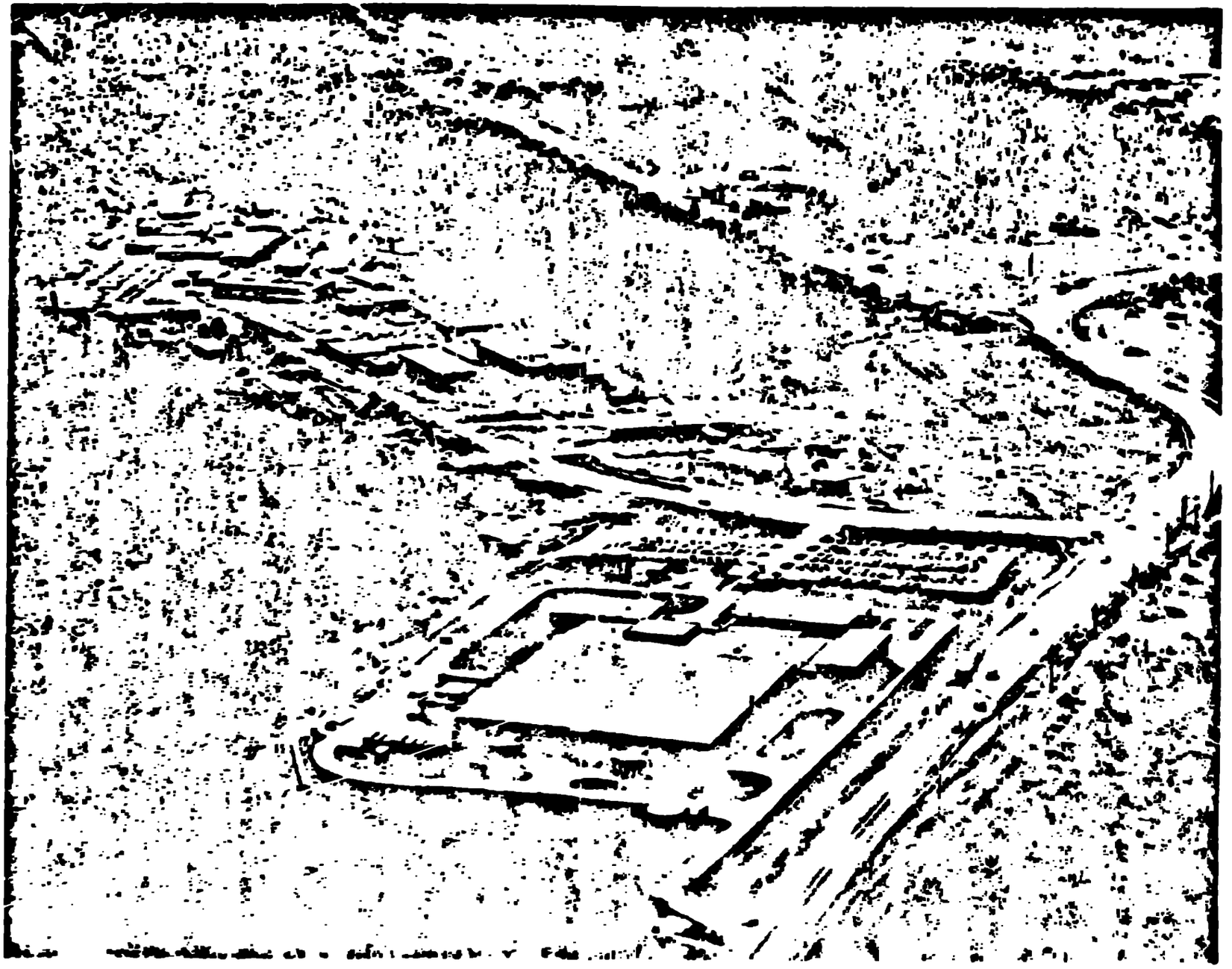

Figure 1. Aerial View of New Plutonium Facility at Los Alamos

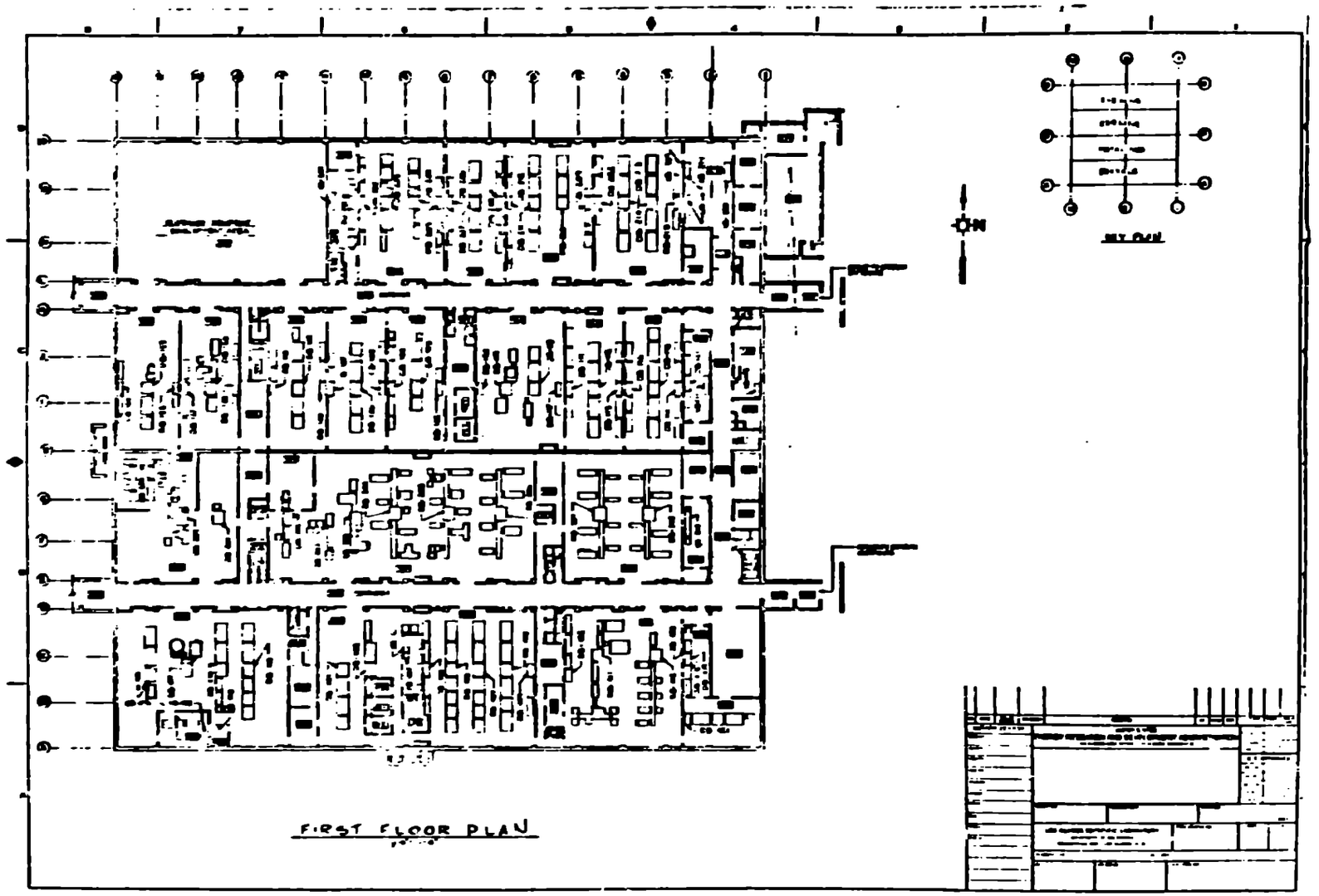

Figure 2. Floor Plan of Process Building at the New Plutonium Facility

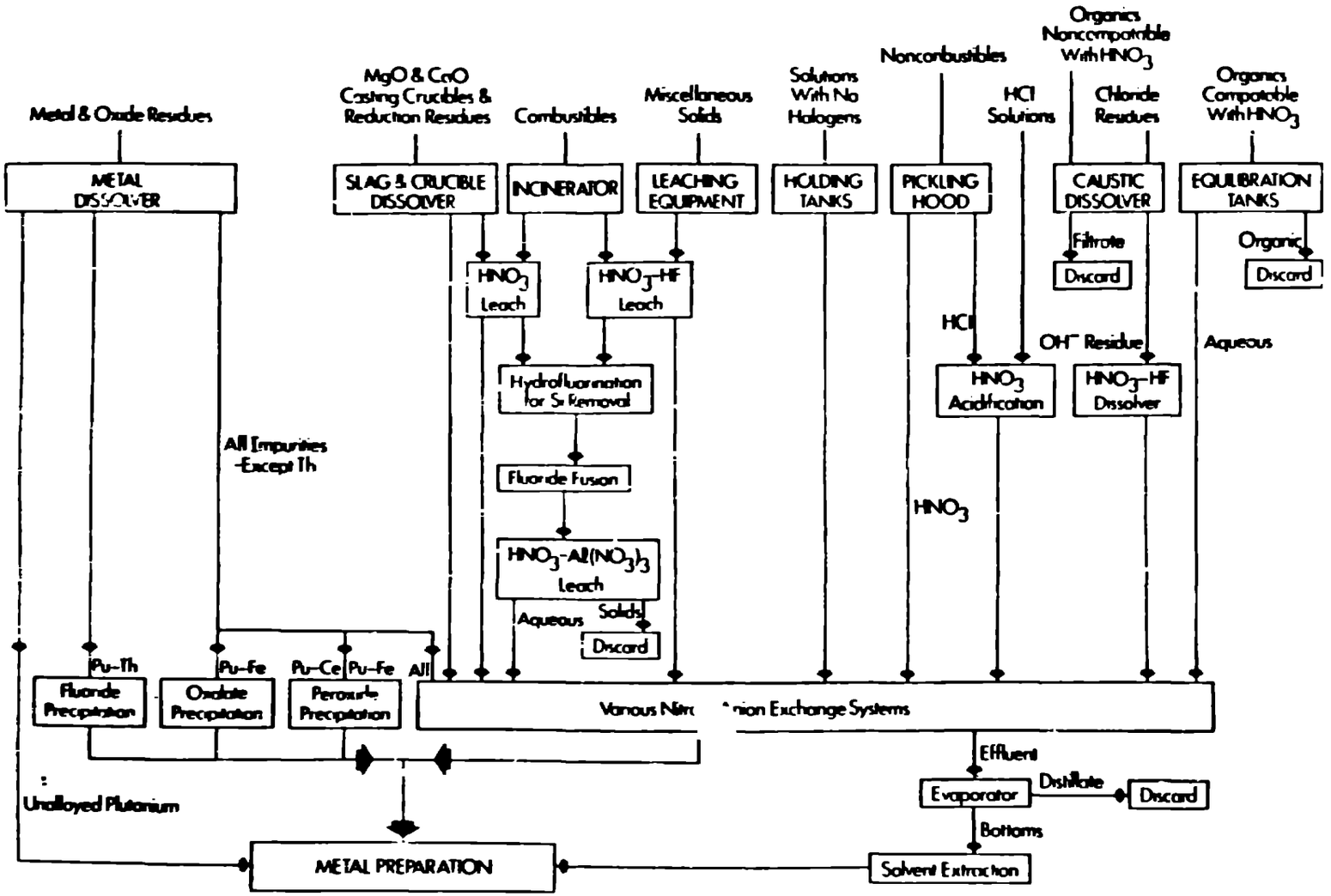

Figure 3.

Flow Of Material In Present Recovery Plant

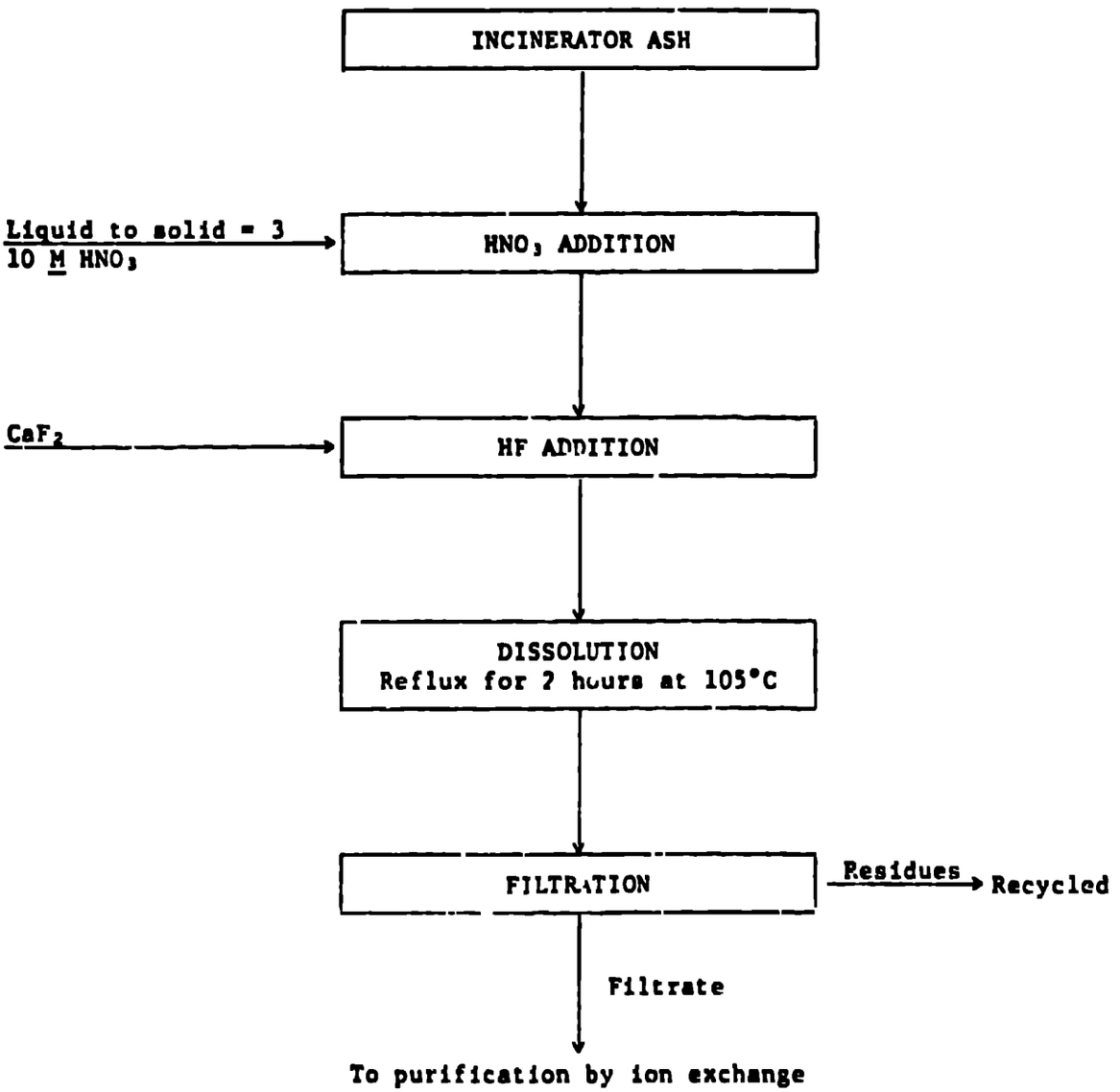

Figure 4. Dissolution of Incinerator Ash

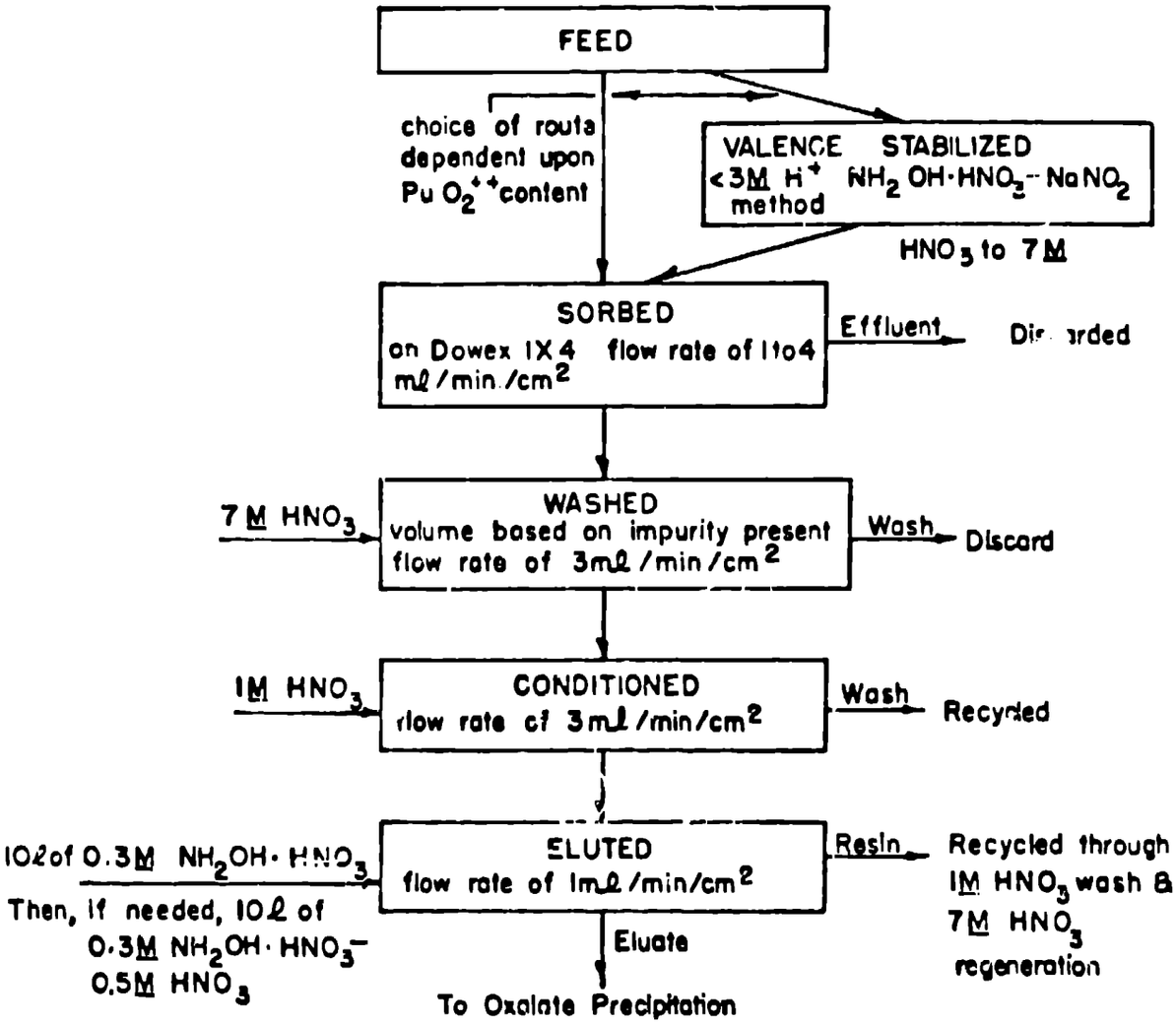

Figure 5. Nitrate Anion-Exchange Processing of Plutonium

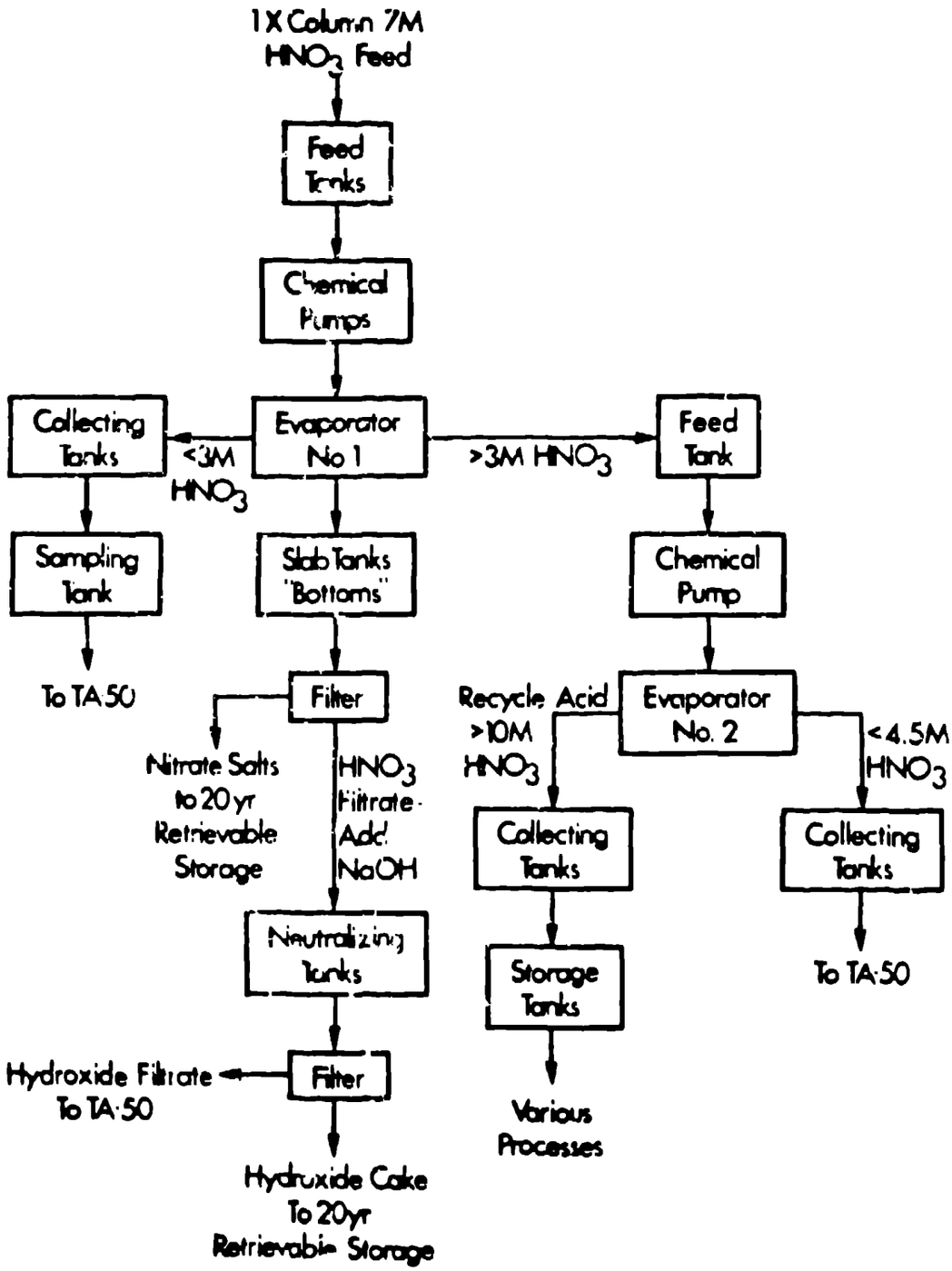

Fig. 6. Evaporation of Nitric Acid

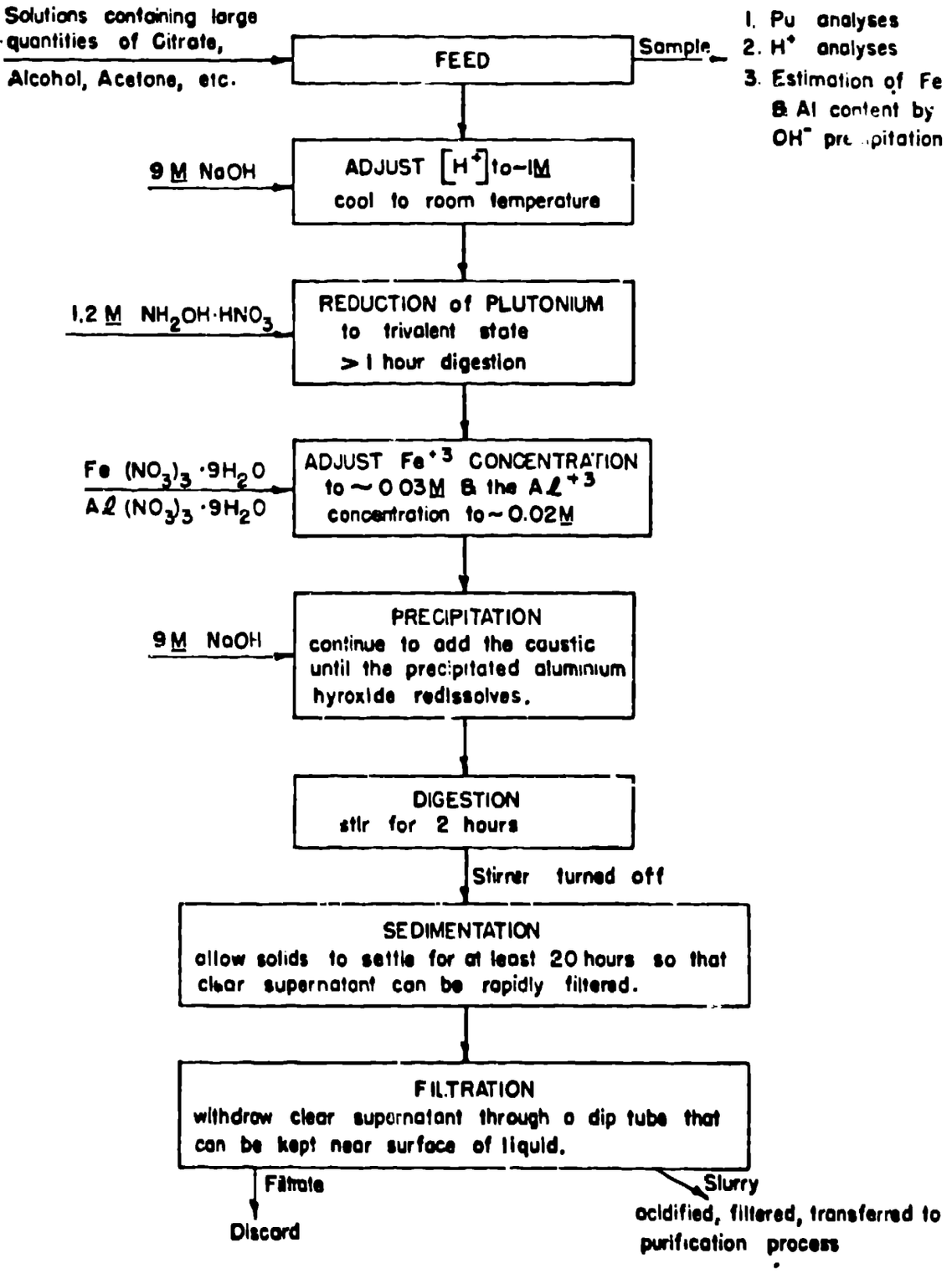

Figure 7. Scavenging of Plutonium by Ferric Hydroxide Carrier Precipitation

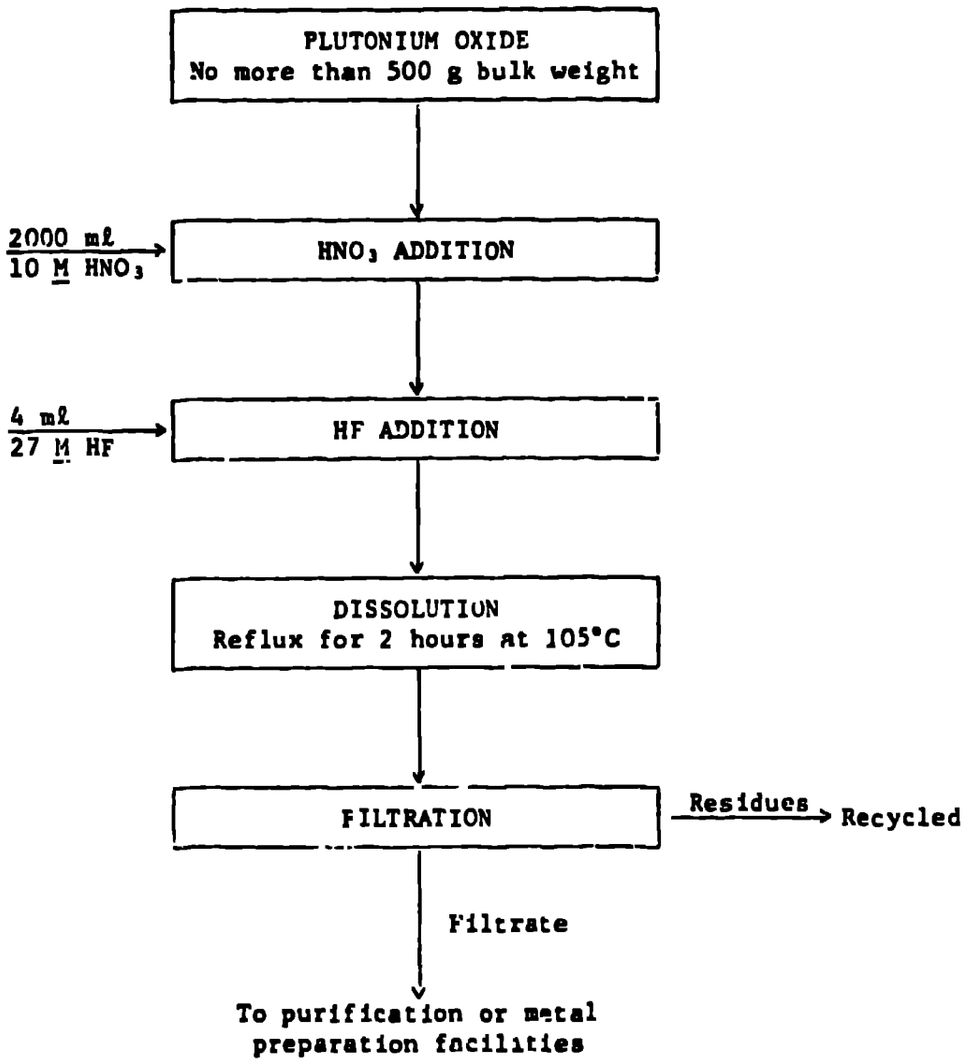

Figure 8. Dissolution of Plutonium Oxide Residues

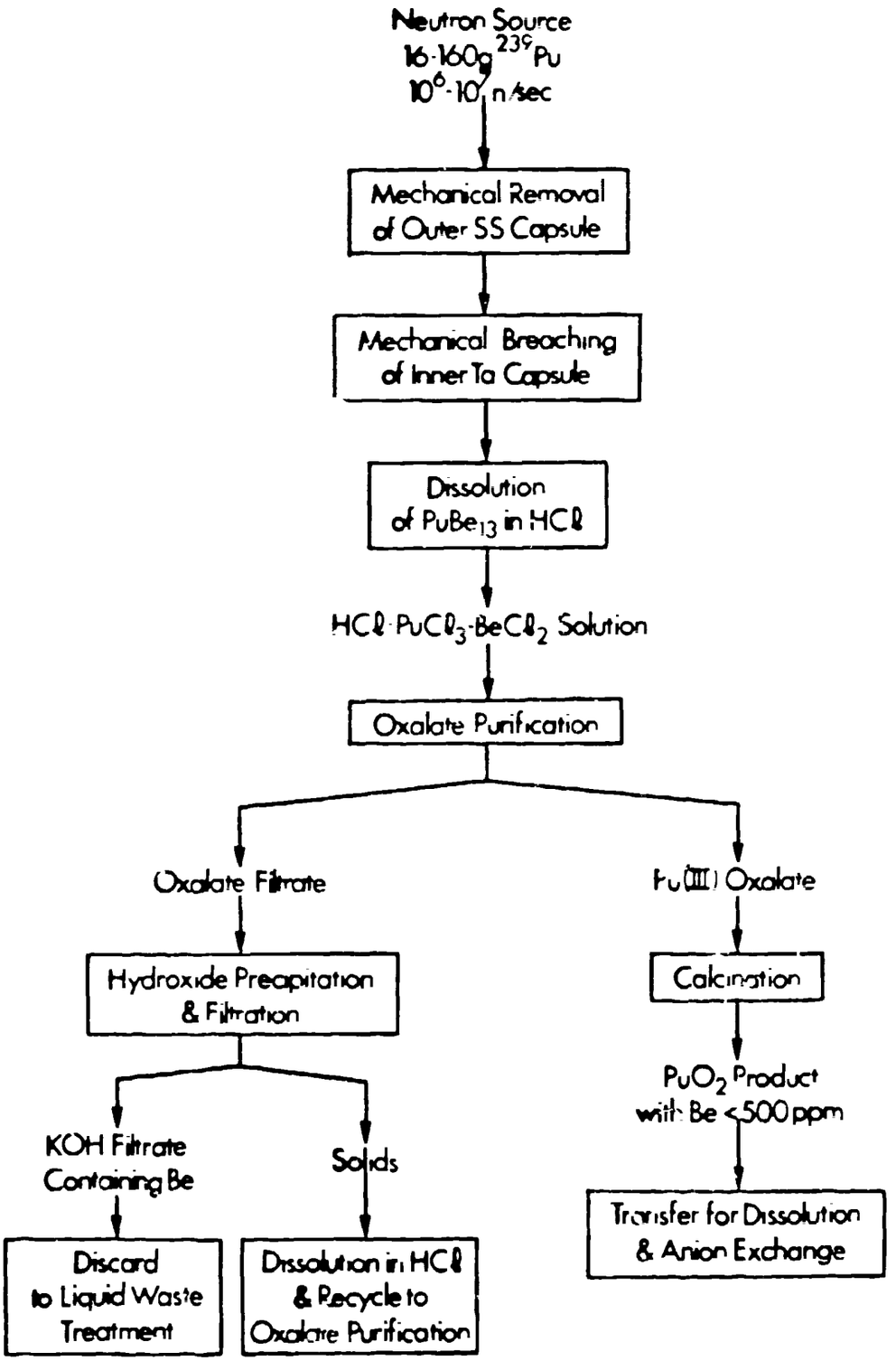

Fig 9. Processing Pu-Be Neutron Sources

Figure 10. Typical Glovebox Line in Plutonium Facility

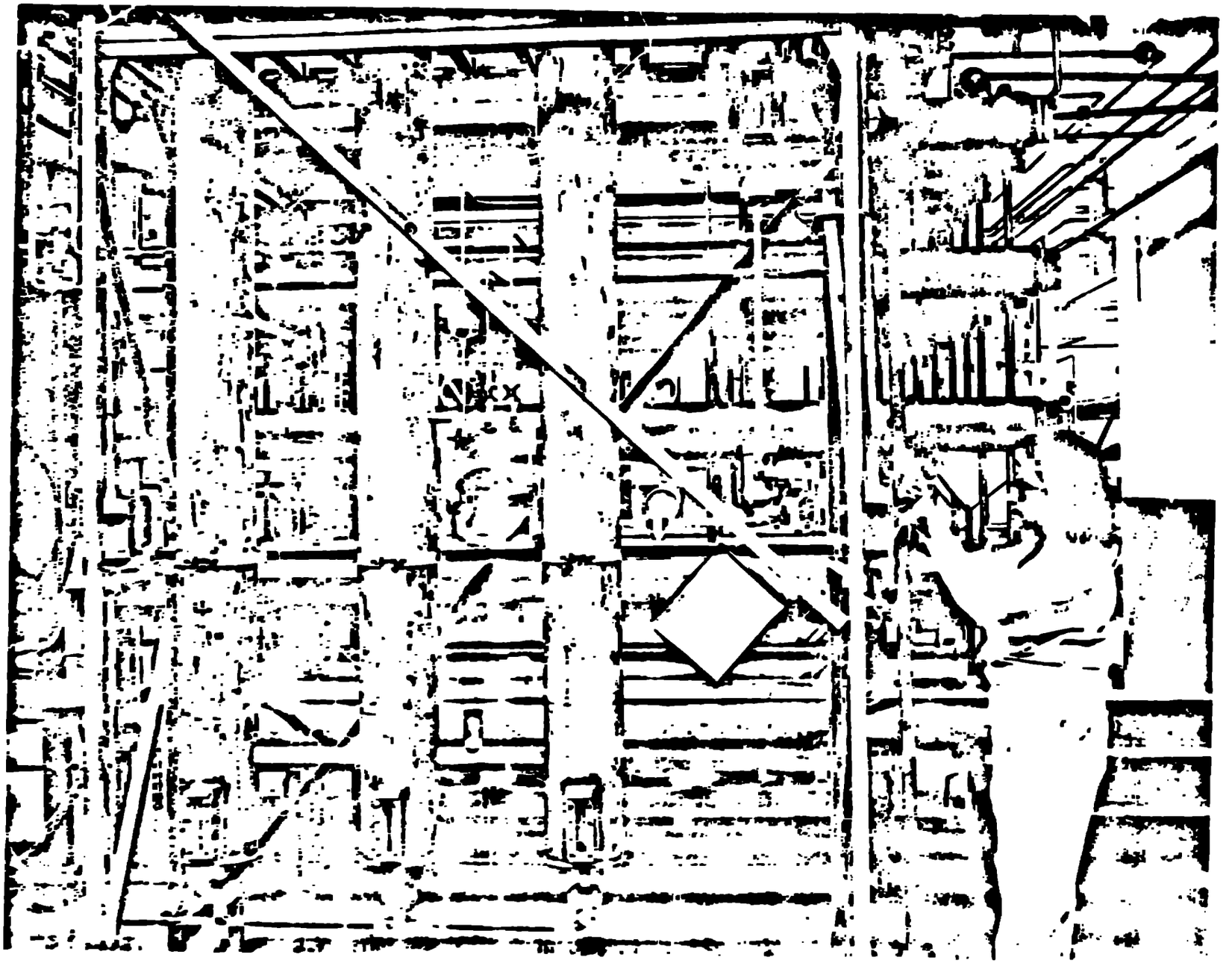

Figure 11. Sampling Station for Discard Solutions

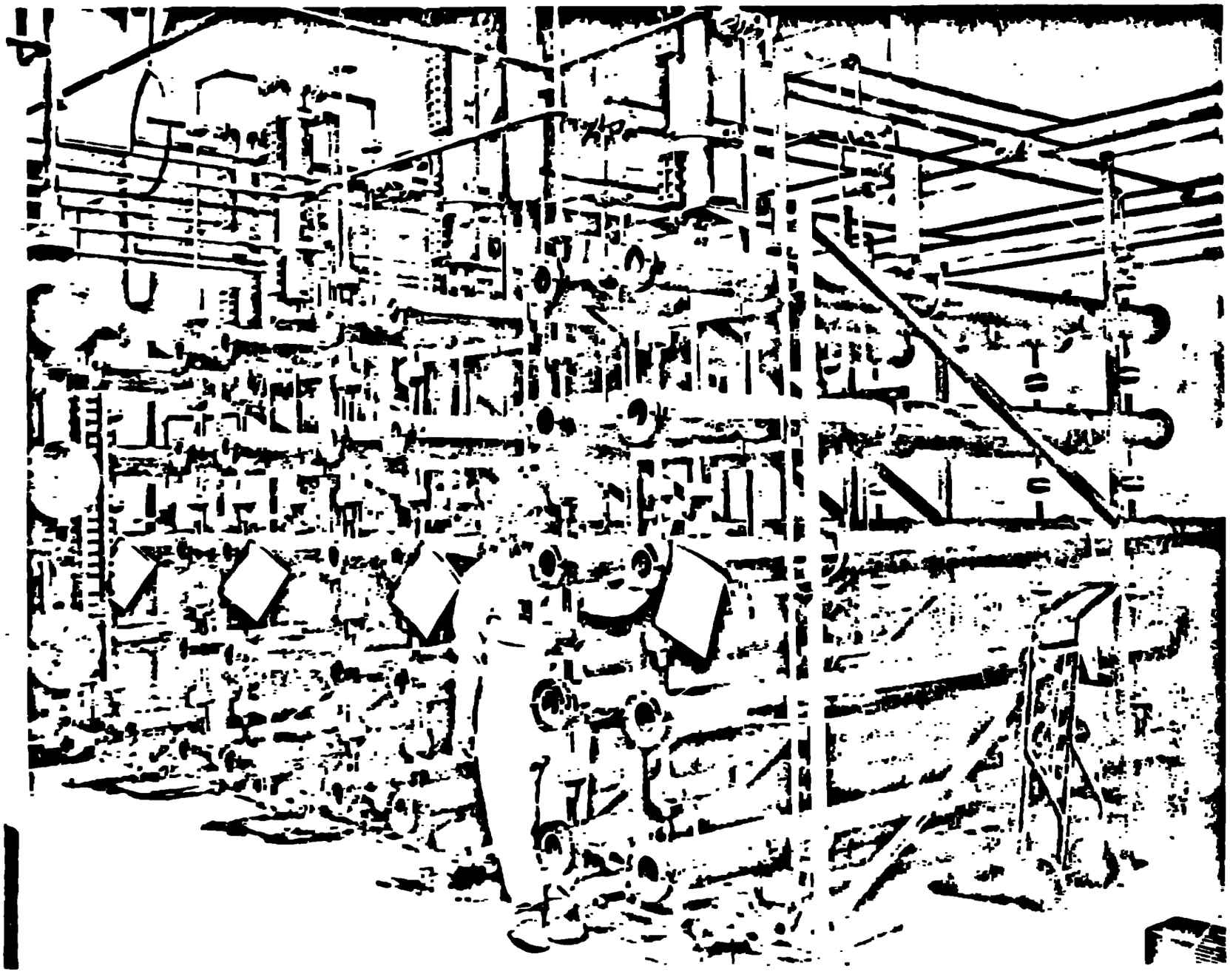

Figure 12. Solution Storage Tanks for Evaporator